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Cadmium, copper and iron in the Scotia Sea, Weddell Sea and Weddell/Scotia Confluence (Antarctica)

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ABSTRACT

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Until recently, little was known about trace metals in the Southern Ocean. Vertical profiles and surface water sections along 49°W exhibit Cd concentrations of 0.2–0.8 nM, increasing with depth, as for phosphate. A linear relationship between Cd and phosphate exists as in other oceans; however, the Cd/P slope at about 0.63–0.65 nM μM^{-1} is much higher than the generally assumed global deep water ratio of about 0.35–0.4 nM μM^{-1}. Dissolved Cu levels range from 1 to 4 nM, increasing with depth, as for silicate. The linear relationship between Cu and silicate shows the same linear trend as in the North Atlantic Ocean, except for the shallow (less than 100 m) Antarctic waters. The South Orkneys shelf appears to be a source of dissolved Cu. Dissolved Fe levels range from 2 to 8 nM in the surface waters. Deep water Fe levels are similar. Over the South Orkneys shelf dissolved Fe is an order of magnitude higher (about 60 nM). Shelf sediments appear to be a major source for Fe; transport of weathered material by ice(bergs) may also contribute Fe to seawater.

INTRODUCTION

From about 1976 many authors reported on the distributions of dissolved metals in seawater. Most investigations focused on the North Pacific and North Atlantic Oceans (Boyle et al., 1976; Martin et al., 1976; Bruland, 1983; and many others). In addition, some work was done in the Arctic Ocean (Moore, 1981, 1983; Danielsson and Westerlund, 1983; Mart et al., 1983; Yeats, 1988). Until recently only one data set existed for the Indian Ocean (Danielsson, 1980). In the Southern or Antarctic Ocean proper, very few data have been available (Orren and Monteiro, 1985; Bordin et al., 1987).

In several studies Cd was found to correlate strongly with phosphate (Boyle et al., 1976; Martin et al., 1976; Bruland, 1980; Knauer and Martin, 1981;

Olafsson, 1983; Bruland and Franks, 1983; Danielsson and Westerlund, 1983; Yeats and Campbell, 1983; Jones and Murray, 1984; Matsunaga and Abe, 1985; Sakamoto-Arnold et al., 1987). At any given station the relation between Cd and phosphate is usually very strong, and often there is a breakthrough between surface waters and deep waters (Boyle, 1988). The correlation between Cd and phosphate also holds to some extent in lateral surface water sections of the Pacific Ocean (Boyle et al., 1981). Kremling and Pohl (1989) reported a very strong relationship in winter along a surface transect in the North-East Atlantic Ocean. However, in summer, when phosphate was almost depleted, Cd concentrations ranged from 4 to 50 pM, and the relationship ceased to exist. This also suggested that phosphate becomes depleted before Cd.

The vertical profiles of Cu often resemble those of silicate; however, Cu deviates somewhat from silicate as it is also strongly influenced by local input sources in surface and bottom waters, combined with intensive scavenging throughout the water column (Boyle et al., 1977; Bruland, 1980; Bruland and Franks, 1983).

It is well known that the trace metals Cd and Cu (as well as Ni and Zn) are involved in marine biogeochemical cycles (Morel and Hudson, 1985). In oligotrophic surface waters of the major ocean gyres these metals and the nutrients often are strongly depleted. In the Antarctic region there is, however, a surplus of nutrients in the surface waters. These high nutrient levels in Antarctic surface waters, combined with the low standing stocks of phytoplankton, are often referred to as the 'Antarctic Paradox' (Tréguer and Jacques, 1986; de Baar et al., 1990).

Fe has been suggested to be a limiting element in phytoplankton growth (Martin and Fitzwater, 1988; Martin and Gordon, 1988; Martin et al., 1989; Martin, 1990). Recently de Baar et al. (1989, 1990) actually found that, in the Weddell Sea, the Scotia Sea and the intermediate Weddell/Scotia Confluence, Fe always stimulated phytoplankton growth, yet Fe was not the single limiting factor for productivity. Relatively few data are available to date for dissolved Fe in seawater (Gordon et al., 1982; Symes and Kester, 1985; Martin and Gordon, 1988; Martin et al., 1989; Saager et al., 1989). Generally, concentrations range from 0.5 to 5 nM, with even lower values in open ocean surface waters (Martin et al., 1989). For the Southern Ocean there has been no information on dissolved Fe levels.

Here we report on dissolved Cd, Cu and Fe in the Weddell Sea, Scotia Sea and the Weddell/Scotia Confluence, with emphasis on their nutrient relations. Initial results have been reported elsewhere (Nolting and de Baar, 1990). This research was a part of the EPOS (European Polarstern Study) programme organized by the European Science Foundation in close co-operation with the Alfred Wegener Institute for Polar Research.

METHODS

Throughout the procedures only extensively acid-cleaned and -rinsed Teflon and polyethylene labware were used. All reagents were quartz distilled. Samples were collected with 12 well-cleaned modified Teflon-coated Go-Flo samplers (12 l volume) fitted on an all-Teflon-coated stainless steel conductivity–temperature–depth (CTD) rosette frame from 26 November 1988 to 4 January 1989 on board R/V "Polarstern". Surface samples were collected with a rubber zodiac. The rosette was always sent to depths greater than 500 m to flush out any possible contamination, and during the up-cast the samplers were closed at selected depths. Upon recovery, the samplers were mounted outside a Class-100 clean-air laboratory container. The samplers were connected with all-Teflon (PTFE, FEP) tubes leading the water inside (through the wall) the container where it was fed through all-Teflon filtering units. Under nitrogen pressure the seawater was filtered over 0.4 μm acid-soaked Nucleopore filters. The first few litres of seawater were discarded and subsequently a precleaned 1 l polypropylene bottle was rinsed three times with the sample and then filled with the filtered seawater (Saager et al., 1989). Thereafter the samples were acidified inside laminar flow benches with 1 ml of 12 N HCl, packed again in plastic bags and stored for analysis. Surface samples were not filtered but were acidified, and were processed as described below (Nolting, 1986). After a few days the seawater samples were subjected to an ammonium pyrrolidine dithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) Freon extraction in Teflon separatory funnels, back-extracted in HNO_3 and stored in 30 ml Teflon flasks (Danielsson et al., 1978, 1982). Using 500 ml of seawater sample and a final back-extraction volume of 5 ml, a concentration factor of 100 was obtained. The flasks were stored in a refrigerator until analysis in the home laboratory, when the element concentrations in the extracts were determined with a Perkin–Elmer 5100 Zeeman AAS, using the platform technique against standards in 0.1 N HCl. Analytical precision for six replicates was 10.5% for Fe, 2.2% for Cu and 6.2% for Cd. Blanks were 0.5 nM for Fe, 0.16 nM for Cu and 0.006 nM for Cd, and were corrected for. In 1989 we participated successfully with this method in the seawater trace metal certification programme CRM-402 of the EEC (Community Bureau of Reference (BCR), 1991).

Analyses of nutrients and chlorophyll *a* were done on board ship with standard methods (EPOS-Leg 2, 1989).

RESULTS

Hydrography

The EPOS 2 programme focused on the interaction of physical, chemical and biological processes at the receding ice-edge (Hempel et al., 1989). Sev-

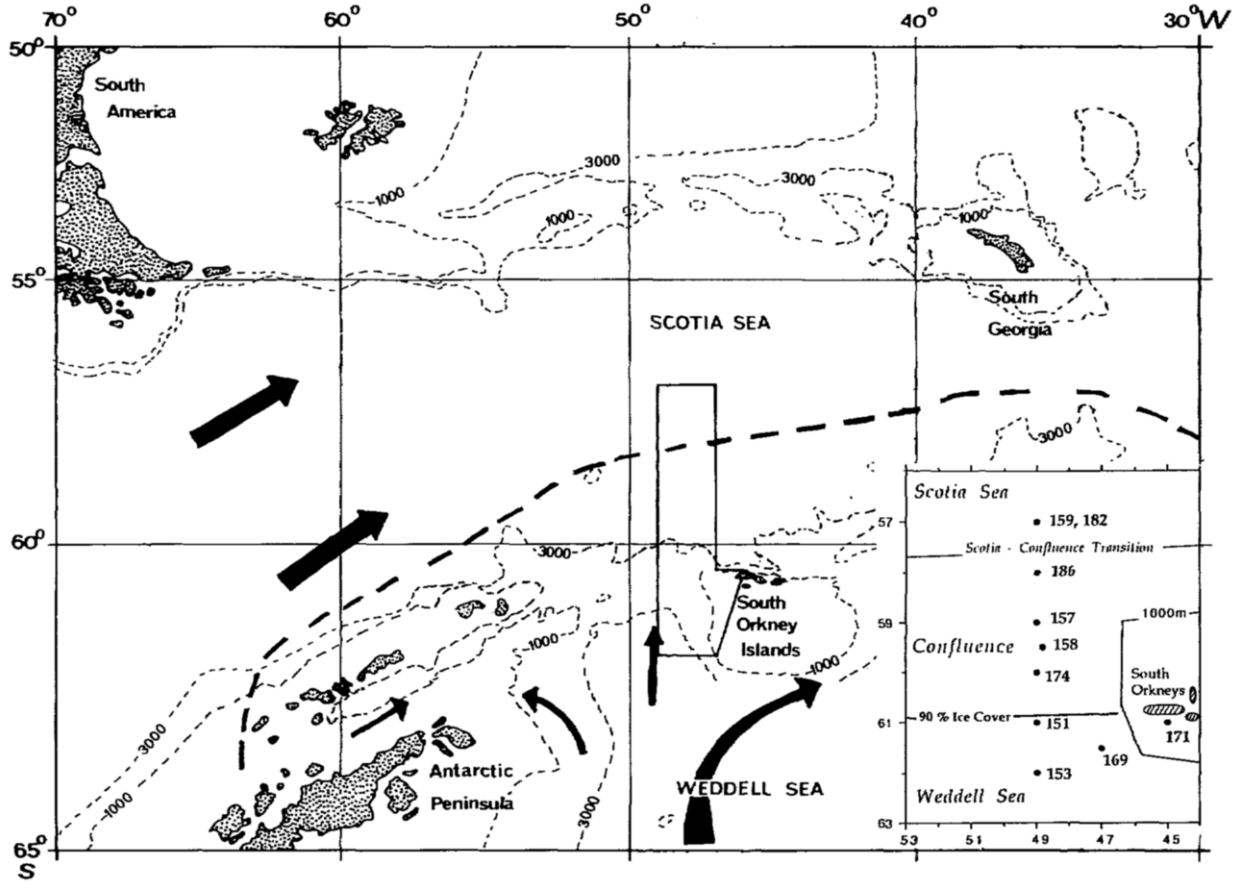

Fig. 1. The Scotia Sea as part of the Antarctic Circumpolar Current, the Weddell Sea and the Scotia/Weddell Confluence. The research rectangle is largely downstream of the Antarctic Peninsula and just west of the South Orkney Islands. Inset: station locations. During the 7 week expedition the ice edge was retreating southwards; the 90% ice cover reflects the ice condition when stations were occupied.

TABLE 1

Sampling depth, hydrography, nutrients and trace metal results of EPOS Stations 153, 159 and 171 (data for other stations available on request)

Depth (m)	Potential temperature (°C)	Salinity	Cu (nM)	Cd (nM)	Fe (nM)	NO_3 (μM)	PO_4 (μM)	Si (μM)
Station 153, 61°59.7'S, 48°59.6'W								
−10	−1.809	34.305	4.17	0.40	9.86	30.9	2.01	76.5
−20	−1.809	34.305	3.48	0.47	6.45	30.9	2.00	77.3
−40	−1.813	34.313	2.85	0.40	(10.68)	31.0	2.01	77.3
−60	−1.810	34.346	2.93	0.43	7.63	31.2	2.02	77.9
−80	−1.798	34.368	2.74	0.43	3.49	31.5	2.03	78.0
−100	−1.743	34.402	4.38	0.41	8.73	31.7	2.04	79.2
−120	−1.499	34.455	6.44	0.50	8.67	31.7		82.5
−150	−1.102	34.496	5.24	0.56	6.84	32.9	2.14	88.0
−400	−0.300	34.662	4.04	0.55	6.68	34.3	2.26	108.4
−600	−0.330	34.676	4.17	0.60	6.00	34.5	2.26	114.3
−1500	−0.021	34.676	5.37	0.52	8.05	34.1	2.26	125.2
Station 159, 57°00.1'S, 48°23.9'W								
−10	1.247	33.782	(4.08)	0.29	2.41	27.7	1.77	27.7
−20	1.223	33.799	2.69	0.31	1.71	27.9	1.76	27.4
−30	1.215	33.800	2.46	0.31	2.52	27.9	1.76	27.4
−40	1.204	33.801	2.05	0.32	1.71	28.0	1.75	27.1
−60	−0.204	33.851	1.64	0.37	3.54	29.1	1.87	26.1
−80	−0.410	33.890	(3.28)	0.52	3.01	29.9	1.91	31.5
−100	−0.374	33.949	2.93	0.65	4.12	31.4	2.01	32.8
−120	−0.259	34.012	1.81	0.58	3.34	32.4	2.06	38.2
−150	0.515	34.150	1.97	0.71	1.76	35.5	2.24	46.5
−180	1.162	34.257	1.16		1.57	37.1	2.29	54.8
−200	1.681	34.360	2.19	0.77	2.71	38.1	2.34	61.4
−250	1.614	34.407	2.23	0.76	2.46	38.2	2.40	66.2
−300	1.607	34.421	(3.32)	0.70	2.38	38.3	2.43	
−400	1.925	34.551	2.17	0.80	3.98	38.3	2.43	76.8
−450	2.037	34.576		0.81	4.24	38.1	2.40	80.6
−500	2.117	34.613	2.57	0.75	3.22	37.7	2.38	82.4
−600	1.971	34.639	2.57	0.71	2.41	37.5	2.36	85.2
−800	1.893	34.690	3.04	0.69	2.50	36.7	2.32	93.9
−1000	1.719	34.702	3.15	0.70	2.64	36.5	2.29	100.4
−1250	1.534	34.713	(6.63)	0.72	3.17	36.1	2.26	102.7
−1500	1.285	34.712	(1.79)	(0.38)	(2.01)	36.1	2.26	106.2
−1750	1.017	34.712	(4.02)	0.67	(3.68)	35.8	2.26	112.8
−2000	0.830	34.712	3.10	0.63	2.50	36.1	2.27	119.2
−2250	0.622	34.703	3.32	0.69	2.48	36.2	2.27	123.8
−2500	0.461	34.693	3.69	0.81	2.55	36.3	2.28	125.3
−2750	0.300	34.687	3.83	0.69	1.58	36.4	2.28	124.8
−3000	0.157	34.682	3.50	0.62	(5.67)	36.1	2.29	124.5
−3250	0.039	34.677	3.06	0.59	4.19	36.3	2.30	123.2
−3500	−0.078	34.669	(4.91)	0.60	3.19	35.9	2.30	121.7
−3750	−0.150	34.667	3.31	0.66	4.00	36.3	2.30	121.5
−3881	−0.194	34.660	3.94	0.65	3.43	36.1	2.29	121.0
−3921	−0.205	34.665	3.40	0.62	1.81	36.2	2.29	121.2
−3931	−0.210	34.662	3.55	0.55	3.00	36.1	2.30	120.8

TABLE 1 (continued)

Depth (m)	Potential temperature (°C)	Salinity	Cu (nM)	Cd (nM)	Fe (nM)	NO_3 (μM)	PO_4 (μM)	Si (μM)
Station 171, 60°51.8'S, 45°22.4'W								
−10	−1.233	33.741	9.80	0.76	66.09	28.7	1.82	80.8
−20	−1.231	33.719	1.75	0.54	48.71	28.7	1.76	80.3
−50	−1.274	34.024	2.11	0.66	59.05	28.8	1.93	86.4
−100	−1.628	34.125	10.16	0.60	50.91	31.8	2.06	88.2
−150	−1.620	34.208	8.66	0.64	58.30	32.9	2.09	91.8
−170	−0.546	34.138	16.47	0.65	19.97	33.1	2.13	92.0
−217	−0.496	34.513	11.54	0.76	64.41	34.9	2.34	113.9
−221	−0.447	34.516	4.80	0.66	45.39	34.7	2.36	114.5

Values in parentheses are suspected to be contaminated. At Station 159 (1500 m) the anomalous Cd and Cu values suggest that the Go-Flo closed at the wrong depth (all nutrient values from separate samplers closed at the same depth would still be correct; potential temperature and salinity are from CTD records).

eral north–south sections were made from 57°S to 62°S along the 49°W meridian from open waters in the north through the ice-edge to the south, well into the completely ice-covered Weddell Sea (Fig. 1). The most northerly part of the research area is the Scotia Sea, which belongs to the Antarctic Circumpolar Current proper. In the ice-covered southern part, the Weddell Sea is characterized by the Weddell Gyre, which here flows northeastward. The intermediate Confluence area is the dynamic and complex mixing zone between the two current systems. As a result, the hydrography of the Confluence stations in our section can be characterized as dynamic or even slightly chaotic (Cederlöf et al., 1989). All hydrographic data can be found in the EPOS-Leg 2 data report (1989).

The results of vertical profiles for Cd, Cu, Fe and nutrients at some stations are listed in Table 1, and data for unfiltered surface water samples collected with the zodiac are given in Table 2.

Trace metals: vertical profiles

Cd

Vertical profiles of Cd (Fig. 2) show the 'nutrient type' increase with depth as reported elsewhere (Bruland, 1980; Yeats and Campbell, 1983). There are, however, remarkable differences. In surface waters of the Pacific Ocean (Bruland, 1980) and the Atlantic Ocean (Bruland and Franks, 1983; Yeats and Campbell, 1983; Joint Global Ocean Flux Study, unpublished results, 1989) both Cd and phosphate are very strongly depleted down to levels as low as approximately 0.01 nM for Cd or less than about 0.04 μM (detection limit) for phosphate. In the Southern Ocean surface water, concentrations are about 0.4 nM for Cd and 1.8–2.0 μM for phosphate (the above-mentioned 'Antarc-

TABLE 2

Station number and latitude, chlorophyll *a* content, salinity nutrient values and trace metal results for unfiltered surface water samples collected from the zodiac away from the R/V "Polarstern"; also listed are values for those stations where also filtered seawater was collected at 10 m depth with the Go-Flo samplers on the rosette system (the general good agreement between unfiltered surface water and filtered water at 10 m depth underlines the reliability of the various sampling methods)

Station no.	South	Chl *a* ($\mu g\,l^{-1}$)	Salinity	Si (μM)	NO_3 (μM)	PO_4 (μM)
151	60.59	0.36	34.18	77.20	30.80	2.06
153	62.00	0.20	34.30	76.50	30.90	2.01
154	61.51	0.16	34.29	76.50	31.60	2.04
156	61.00	0.51	34.08	76.40	31.70	2.01
157	59.00	0.14	33.55	58.10	22.40	1.26
158	59.27	2.34	33.48	68.60	25.30	1.49
159	57.00	0.19	33.78	28.60	27.70	1.83
169	61.30	0.61	33.72	78.90	27.40	1.82
171	60.51	1.00	33.74	80.80	28.70	1.82
172	59.00	0.85	33.60	60.20	21.10	1.37
173	59.31	2.41	33.45	63.70	20.20	1.34
174	60.00	1.04	33.86	81.50	28.90	1.85
175	60.31	0.70	33.79	79.80	27.40	1.57
176	60.58	1.12	33.86	74.00	29.30	1.88
177	61.29	0.39	33.97	78.00	29.40	1.99
182	57.00	0.55	33.80	15.00	26.40	1.60
186	58.00	0.19	33.83	32.90	27.00	1.76
189	59.30	1.21	33.60	62.40	19.70	1.37
192	61.00	0.52	33.81	73.00	27.70	1.86
194	61.45	0.28	34.02	79.90	30.10	1.96

Station no.	Cu (0 m) (nM)	Cu (10 m) (nM)	Fe (0 M) (nM)	Fe (10 M) (nM)	Cd (0 m) (nM)	Cd (10 m) (nM)
151	4.63	3.80	4.39	8.55	0.58	0.56
153		4.17		9.86		0.40
154	2.55		4.39		0.62	
156	2.52	3.59	4.21	4.35	0.61	0.59
157	3.31	2.77	5.56	5.66	0.60	0.47
158	3.53	4.69	4.82	5.30	0.48	0.41
159	2.54	4.08	7.55	2.41	0.42	0.29
169	3.10	3.23	5.30	3.17	0.61	0.56
171		9.80		66.09		0.76
172	2.98		8.89		0.51	
173	3.13		6.94		0.53	
174	2.00	2.65	5.07	7.81	0.53	0.58
175	1.83		3.32		0.64	
176	1.87		7.43		0.50	
177	2.08		2.87		0.45	
182	1.91	2.44	3.05	2.56	0.41	0.17
186		1.94		3.66		0.39
189	4.39		8.58		0.99	
192	2.02		18.35		0.56	
194	1.87		2.90		0.47	

All data are reported. There are no suspect values. At some stations only one type of sample was collected (i.e. unfiltered surface water or filtered water at 10 m depth).

tic Paradox'). Maximum Cd concentrations are found at about 1000 m in Pacific and North Atlantic waters, whereas in Antarctic waters maximum values are reached already at 100–200 m depth. Deep water concentrations of Cd in the Antarctic (0.7–0.8 nM), are somewhat lower than those found in

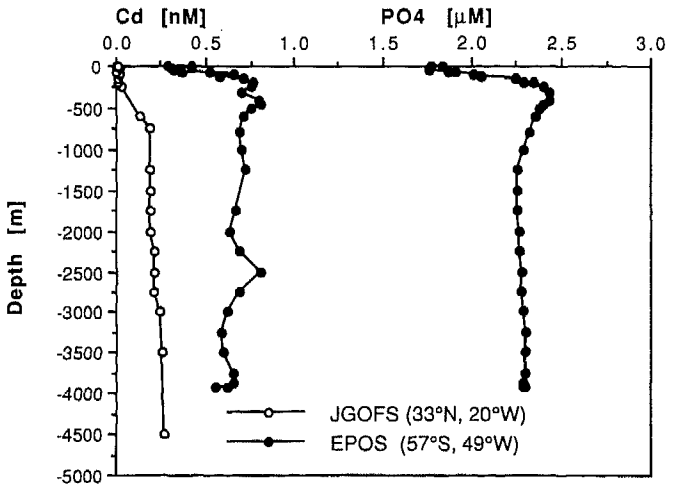

Fig. 2. Vertical profiles of dissolved Cd (nM) and phosphate (μM) at EPOS Station 159 (57°S, 49°W) in the Scotia Sea and, for comparison, Cd (nM) at JGOFS 1989 station in the Northeast Atlantic Ocean (33°N, 20°W).

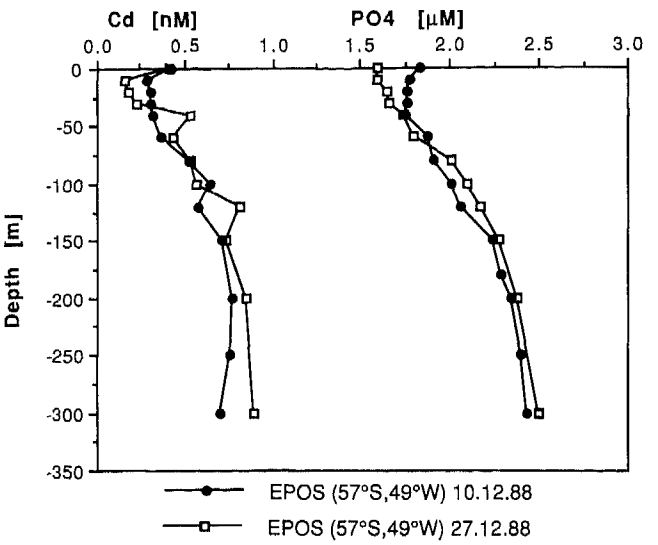

Fig. 3. Minor changes in the upper 300 m over a 17 day interval. Vertical profiles of dissolved Cd (nM) and phosphate (μM) at EPOS Station 159 (57°S, 49°W; 10 December 1988) and EPOS Station 182 (57°S, 49°W; 27 December 1988) in the Scotia Sea.

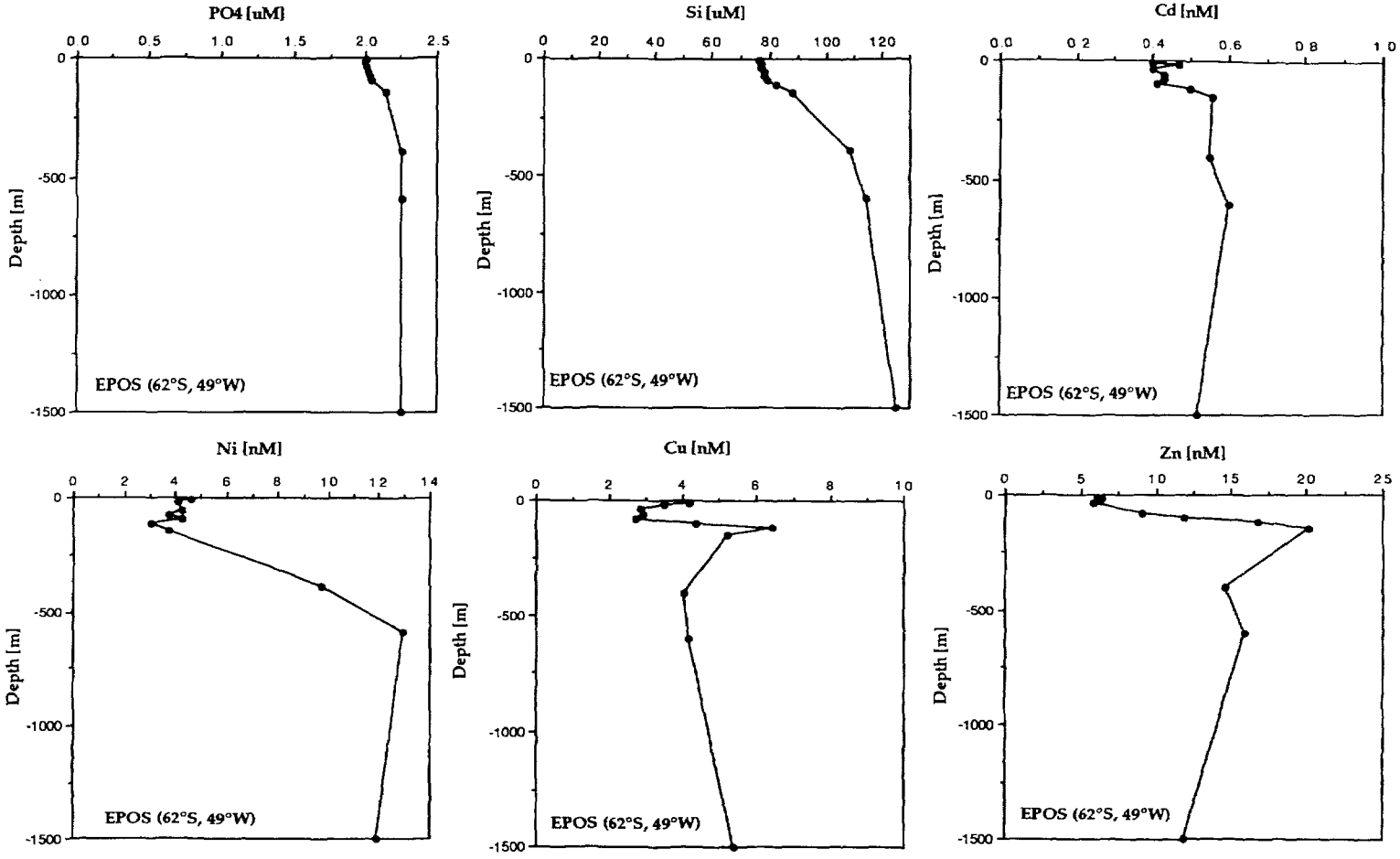

Fig. 4. Vertical profiles at ice-covered EPOS Station 153 (61°S, 49°W). The nutrients phosphate and silicate as well as the metals Cu, Cd, Ni and Zn exhibit distinct gradients in the surface layer directly under the ice. Uptake of Zn, Cd, Ni (and Cu) by ice-algae may, in combination with the poor vertical mixing, lead to the surface minima.

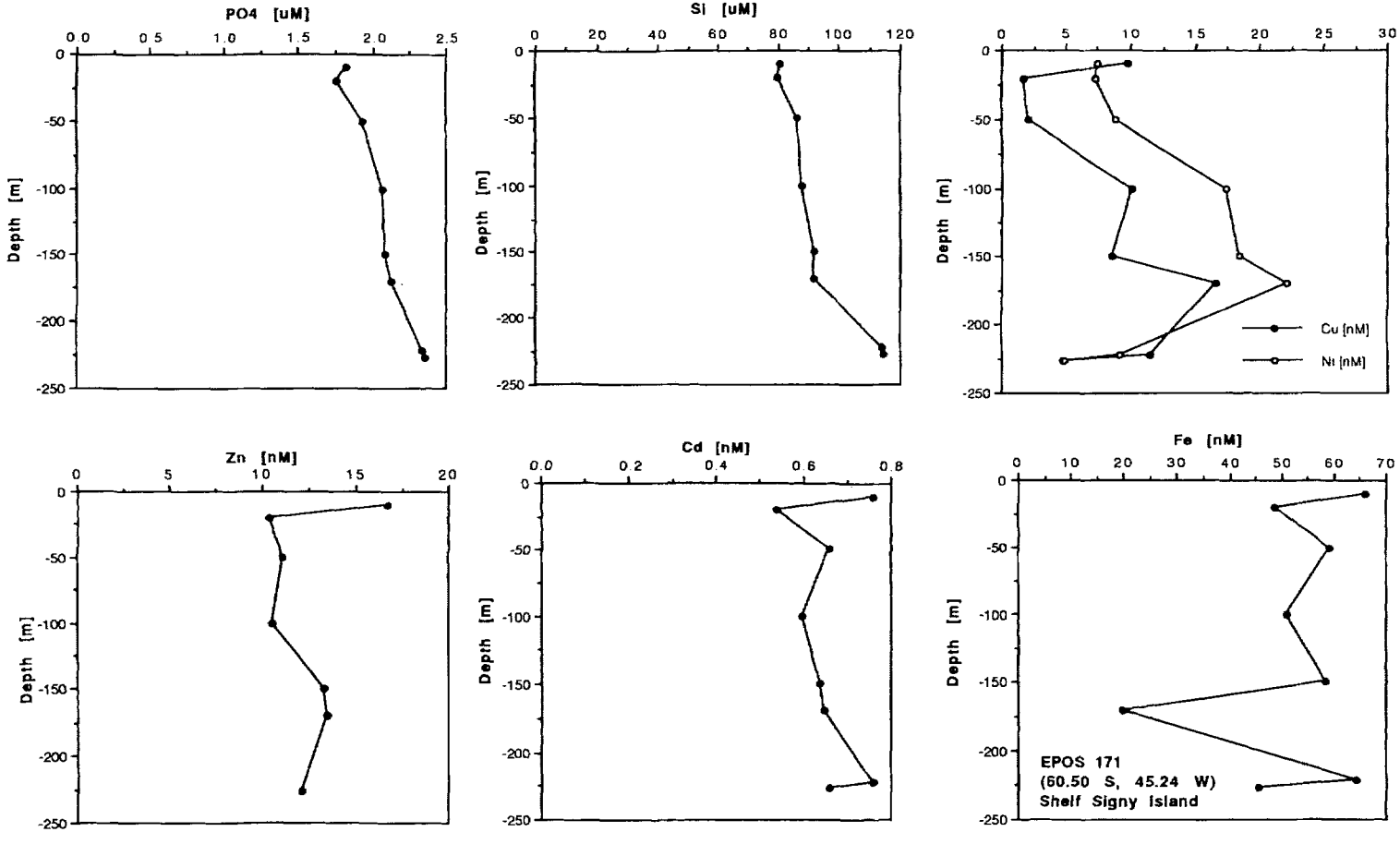

Fig. 5. Vertical profiles at EPOS Station 171 (60.50°S, 45.24°W) on the shelf of the South Orkney Islands close to Signy Island. Water column depth was 235 m.

the North Pacific but are a factor of four higher than those found in North Atlantic and Arctic deep waters (Danielsson and Westerlund, 1983; Yeats and Campbell, 1983; Danielsson et al., 1985). Orren and Monteiro (1985) reported deep water Cd concentrations in the Atlantic–Indian sector of the

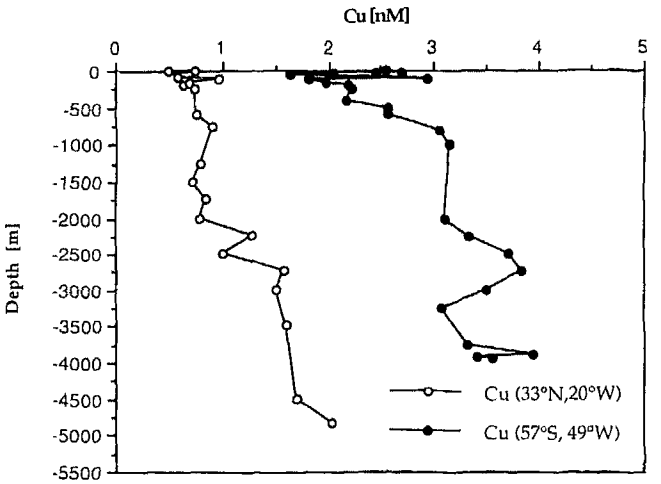

Fig. 6. Vertical profile of dissolved Cu (nM) in the Scotia Sea at EPOS Station 159 (57°S, 49°W) and, for comparison, Cu (nM) at JGOFS 1989 station in the Northeast Atlantic Ocean (33°N, 20°W). Values suspected of contamination are excluded.

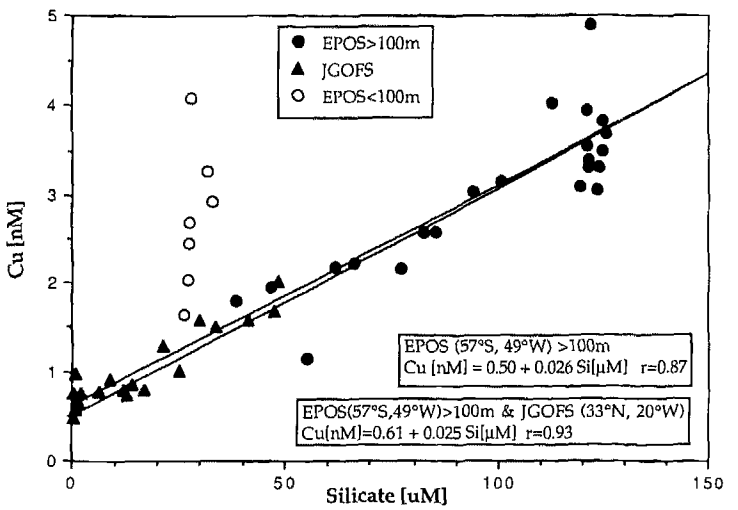

Fig. 7. The linear relationship between Cu and silicate throughout the Atlantic into the Antarctic Ocean, with exception of (open symbols) Antarctic surface waters shallower than 100 m depth. All values of EPOS Station 159 (57°S, 48°W) are used, with the exception of those at 1250, 1500 and 1750 m (Table 1).

TABLE 3

Linear correlation between Cu and H_4SiO_4 along vertical profiles at given stations in the oceans

Region	Latitude	Longitude	Cu (nM) = aSi(μM) + b		r	n	Depth range	Reference
			a(slope)	b(intercept)				
Atlantic Ocean								
Sargasso Sea	~35°N	~64.5°W	0.049	1.02	0.78	21	0–3900	Jickells and Burton (1988)
Sargasso Sea	34°N	66°W	0.041	1.12	0.93	10	0–2962	Bruland and Franks (1983)
Sargasso Sea	35.39°N	71.53°W	0.044	0.82	0.90	11	500–3000	Hanson et al. (1988); Si from Sakamoto-Arnold et al. (1987)
NE Atlantic	33°N	20°W	0.023	0.67	0.88	21	0–4500	JGOFS, this work
Southern Ocean								
Scotia Sea	57°S	49°W	0.026	0.50	0.87	29	100–4000	This work
Drake Passage	60.46°S	63.26°W	0.012	0.84	0.96	10	0–1850	Martin et al. (1990b)
Marion Isl.	~50°S	~33°E	(no relation between Cu and Si at any of three stations)					Orren and Monteiro (1985)
Atlantic/Indian	67.20°S	28°E	(no relation between Cu and Si at this station)					Orren and Monteiro (1985)
Indian Ocean								
NW Indian (three stations)	~68°E	~0–20°N	0.024	0.73	0.94	15	150–3000	Danielsson (1980)
NW Indian Upwelling	22.30°N	60.40°E	0.019	−0.13	0.95	9	250–3000	Saager et al. (1991)
South Pacific Ocean								
GEOSECS 293	52.40°S	178°W	0.021	1.11	0.91	19	0–5257	Boyle et al. (1977)
North Pacific Ocean								
GEOSECS 202,219, 226,340,345			0.029	(reported ratio at several stations)				Boyle et al. (1977)
H-77	42.31°N	144.59°W	0.012	0.73	0.95	7	0–1000	Bruland (1980)
			(below 1000 m depth Cu increases whereas Si eventually decreases)					
NE Pacific	50°N	145°W	0.006	1.56	0.90	16	0–1500	Martin et al. (1989)
(VERTEX VII, Ocean Station PAPA; below 1500 m Cu continues to increase whereas Si remains constant)								

r, Coefficient of correlation at given n (number of data points). In some instances, only part of the water column was selected, as listed under depth range. The combined relationship of the EPOS Scotia Sea and JGOFS East Atlantic station is shown in Fig. 7.

Southern Ocean to be around 1 nM. Very similar values for both Cd and phosphate were reported for the Drake Passage (Martin et al., 1990b) as well as the Weddell Sea and the Filchner Depression (Westerlund and Öhman, 1991a).

In the Scotia Sea the same site was sampled twice (EPOS Stations 159 and 182) with a time interval of 17 days (Fig. 3). The second sampling appears to reveal slightly lower surface water values as well as higher deep water values for both Cd and phosphate. This is consistent with the notion that during the austral summer, when biological activity increases, phosphate and Cd are removed from the surface and regenerated again below the euphotic zone.

At the most southerly station, EPOS 153, which was well covered with ice, the nutrients and the 'nutrient type' metals Cd, Cu, Ni and Zn all show a distinct increase just below the ice cover (Fig. 4). When covered with ice the

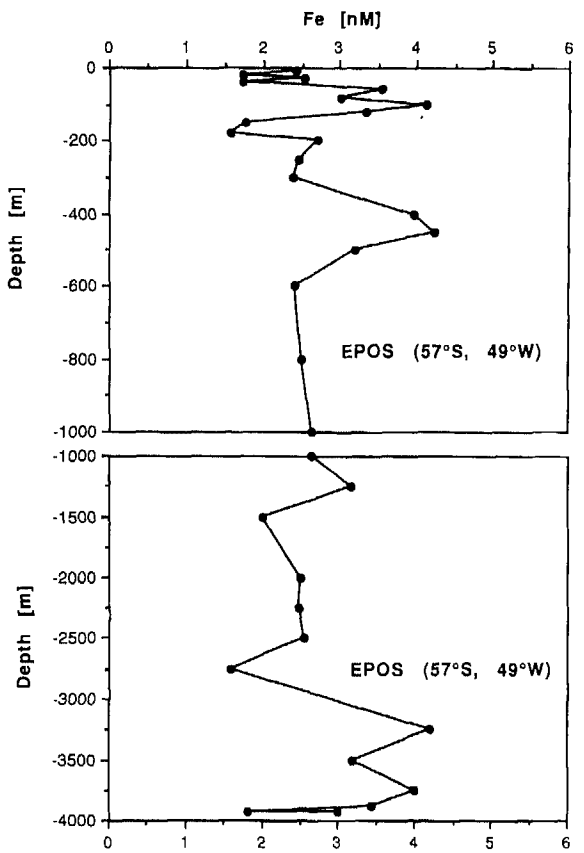

Fig. 8. Vertical profile of dissolved Fe (nM) in the Scotia Sea at EPOS Station 159 (57°S, 49°W). Top: upper 1000 m in detail. Bottom: complete 4000 m water column. Values at 1750 and 3000 m are excluded.

vertical mixing of the surface ocean is greatly diminished. This, combined with the possible uptake of Cd, Cu, Ni and Zn by ice-algae, may explain the distinct surface minima. At the shallow station over the South Orkney shelf, dissolved Cd concentrations are very similar (Fig. 5).

Cu

In analogy with Cd, there is little surface depletion of Cu but otherwise a steady increase to deeper waters to concentrations of 3–3.5 nM (Fig. 6). Within the upper 100 m the Cu concentrations fluctuate considerably. Generally, Cu levels are rather high compared with the North Atlantic Ocean (e.g. Jickells and Burton, 1988). In fact, the highest Cu levels found in the deep waters of the North Atlantic Ocean are still lower than in surface waters of the Antarctic Ocean (Fig. 6). For both stations, however, the same Cu/silicate ratio was found (Fig. 7) except for the upper 100 m of the Scotia Sea station. Excluding the latter values, a linear correlation is found, with a slope of 0.026 nM μM^{-1}. This slope agrees with those published for other World Ocean basins (Table 3). The anomalously high Cu levels found in the surface (0–100 m) Antarctic waters strongly deviate from the overall Cu/Si trend. Such excursions were also found, for example, in the Northwest Indian Ocean near Oman (Saager et al., 1991). There, a relationship between Cu and Si exists only below 250 m depth; the shallow water Cu values were 'too high' to fit the trend (Table 3). The higher Cu values in approximately the upper 100 m at our stations may originate from shelf sources, as indicated by the higher dissolved Cu levels at the station over the South Orkney shelf (Fig. 5).

Fe

In the Scotia Sea (EPOS Station 159) the values of Fe increase from about 2 nM at the surface to about 4 nM at about 100 m depth (Fig. 8); there is then a minimum at about 200 m, an increase again to about 4 nM 400–500 m, and then a decrease to about 2–3 nM, until about 3000 m depth. The bottom water generally has higher Fe levels, at about 4 nM, presumably as a result of inputs from sediments. These Fe concentrations are similar to those observed elsewhere (Gordon et al., 1982; Symes and Kester, 1985; Landing and Bruland, 1987; Martin and Gordon, 1988; Saager et al., 1989). Only in some open ocean surface waters have lower values (below 1 nM) been reported (Martin et al., 1989). Recently, surface waters of the Drake Passage values ranging from 0.16 to 1.6 nM were found (Martin et al., 1990b).

Shelf sediments may (by reductive dissolution) act as a major source for dissolved Fe. This is demonstrated very dramatically by the dissolved Fe profile at EPOS Station 171 on the shelf of the South Orkney Islands (Fig. 5). Throughout the water column, of 235 m depth dissolved Fe is as high as 50–60 nM, about an order of magnitude above dissolved Fe levels at all other (i.e. deep) stations (Nolting and De Baar, 1990). Some other dissolved met-

als, Cu, Zn (and also, to some extent, Cd) and the Si concentrations in the bottom waters are also notably higher at this shelf station than at the deep stations.

Recently, dissolved Fe levels of about 5–7 nM were reported for three samples taken in the Gerlache Strait; these are again considerably higher than at offshore stations (Martin et al., 1990b).

Trace metals: surface water sections

Results of unfiltered surface samples collected with a rubber boat during a transect from 57 to 62°S are shown in Fig. 9. At stations where also a filtered sample was collected at 10 m depth there is good agreement (Table 2). Generally, the parameters fluctuate considerably, as a result of the dynamic hydrography in the region. It should be noted that the sampling was by no means synoptic. Salinity is 33.8 in the Scotia Sea, decreasing to 33.4 in the Confluence and increasing to 34.2–34.4 in the Weddell Sea. Silicate increases from 20 μM in the Scotia Sea to 80 μM in the Weddell Sea, where it remains constant. Phosphate and nitrate concentrations show a similar pattern; they start with high values in the Scotia Sea, decrease in the direction of the Confluence and increase again to the Weddell Sea, where the concentrations are higher than in the Scotia Sea. Despite these differences along the transect, the correlation between phosphate and nitrate is good: $NO_3(\mu M) = 3.83 + 13.38$ $PO_4(\mu M)$, where $r = 0.94$ for $n = 20$. The value of the slope, 13.38, is between the 'typical' Antarctic ratio of 11:1 (Jennings et al., 1984) and the 16:1 Redfield value. Otherwise, neither chlorophyll *a* nor any of the other variables can be related to each other, nor with trace metals, by regression.

In contrast to the nutrient sections, Cd and Cu show a different pattern: they are low in the Scotia Sea, higher in the Confluence and again lower in the Weddell Sea. It should be noted that all surface water samples were unfiltered, which might explain the elevated Cu and Cd levels in the Confluence. Concentrations of Cd ranged from 0.4 nM in the Scotia Sea to 1.0 nM in the Confluence and are around 0.5 nM in the Weddell Sea. The concentration of Cu is about 2.0 nM in the Scotia Sea, about 4.0 nM in the Confluence and about 2.0 nM in the Weddell Sea. It is noteworthy that Cu concentrations are rather high (10 nM) in the vicinity of Signy Island, indicating a flux of Cu from shelf sediments (Heggie et al., 1987). Fe shows the same general trend as Cd and Cu, with higher concentrations in the Confluence and ranging from 2 to 10 nM over the whole transect. An exception is the shelf station near Signy Island, where rather high dissolved Fe concentrations were found (about 60 nM).

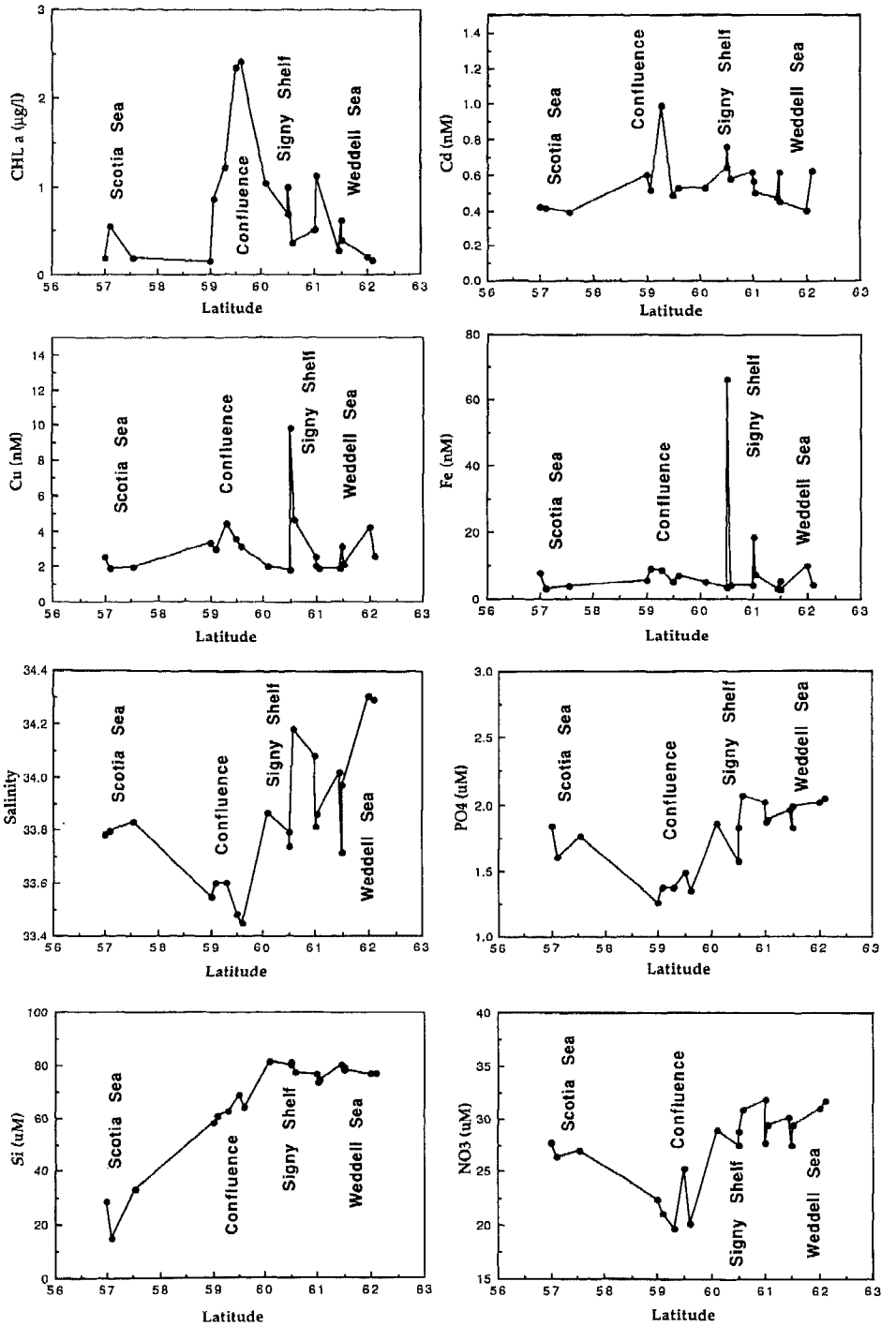

Fig. 9. Lateral north–south sections of the surface waters during EPOS 2. At stations where no surface water sample was collected the 10 m depth value was plotted (Table 2).

DISCUSSION

Currently the Cd–P relationship in deep waters is commonly regarded as remarkably uniform all over the globe (Boyle, 1988). However when surface water values are included, a significant change in slope in the Cd–P relationship has been suggested at a phosphate concentration of about 1.3 μM (Boyle, 1988). Below about 1.3 μM for phosphate (i.e. all surface water data) the Cd–P relationship would have a slope of about 0.21 nM μM^{-1}, passing only slightly below the origin at zero phosphate. Above about 1.3 μM for phosphate the Cd–P relationship would have a slope of about 0.4 nM μM^{-1}, and it passes through the zero-phosphate axis at a Cd concentration of -0.25 nM. These relationships were, however, based on combining mostly North Pacific data sets into one overall correlation. Differences between stations might thus have become obscured. New data sets have just become available.

When plotting phosphate vs. nitrate from EPOS Station 159 and North Atlantic JGOFS Station 36 (sampled in mid-August 1989 at 33°N, 20°W) the Redfield ratio of approximately 16 is found (not shown). On the other hand, when plotting Cd vs. phosphate (Fig. 10) from the same stations (all depths) there appear to be two distinct slopes: 0.194 nM μM^{-1} in the North Atlantic as opposed to a steeper slope of 0.629 nM μM^{-1} for the Antarctic Ocean (Table 4). This would suggest that the commonly used global ratio of about 0.35–0.40 nM μM^{-1} (Boyle, 1988) does not hold in the Antarctic Ocean, or for that matter, the Atlantic Ocean. The ratio found in the Scotia Sea (EPOS Station 159) is supported by data from the Weddell Sea (Fig. 11, EPOS Stations 153 and 156), where we found the same slope of about 0.6 nM

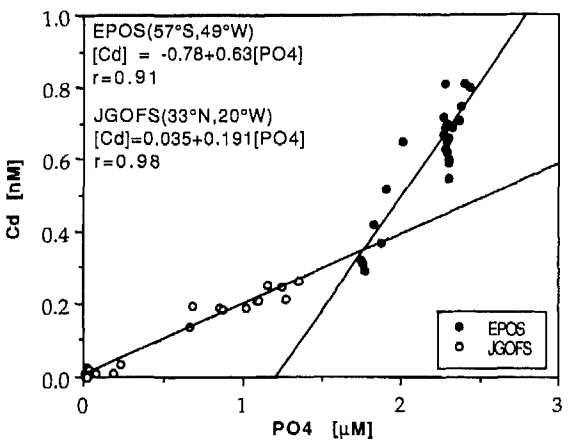

Fig. 10. The different relationships between Cd and phosphate along vertical profiles at two stations in the Scotia Sea (EPOS Station 159) and the Northeast Atlantic Ocean (JGOFS) respectively.

TABLE 4

Linear correlations between Cd and PO_4 along vertical profiles at given stations in the oceans

Region	Latitude	Longitude	Cd (nM) = $aP(\mu M)+b$		r	n	Depth range	Reference
			a(slope)	b(intercept)				
Arctic Ocean								
Arctic Atlantic	*82.31°N*	*43.57°E*	*0.14*	*0.075*		*10*	0–2400	Danielsson and Westerlund (1983)
Atlantic Ocean								
NW Atlantic	34.06°N	66.07°W	0.25	−0.019	0.995	11	0–2962	Bruland and Franks (1983)
NE Atlantic	48.30°N	20.00°W	0.20	−0.004	0.98	8	0–2700	Danielsson et al. (1985)
NE Atlantic	33.00°N	20°W	0.19	0.005	0.98	16	0–4600	JGOFS R.V. 'Tyro' (unpubl.)
Southern Ocean								
EPOS 159	57°S	49°W	0.63	−0.76	0.91	30	0–3931	This work
EPOS 156	61°S	49°W	0.57	−0.62	0.76	17	0–2187	This work
EPOS 153	62°S	49°W	0.56	−0.71	0.87	11	0–1500	This work
Antarctic Atlantic	67°S	28°E	no relation was found ($r<0.03$)					Orren and Monteiro (1985)
Drake Passage	60.46°S	63.26°W	0.65	−0.85	0.986	10	0–1850	Martin et al. (1990b)
Antarctic Indian	54.40°S	63.06°E	0.68		0.801	8	0–3346	Bordin et al. (1987)
Antarctic Indian	61.05°S	66.20°E	0.82		0.775	8	0–3551	Bordin et al. (1987)
Indian Ocean								
NW Indian	14.30°N	67.00°E	0.50	−0.49	0.97	14	100–4000	Saager et al. (1991)
	14.30°N	67.00°E	0.15	−0.054	0.999	4	0–100	
NW Indian	22.30°N	60.40°E	0.87	−1.26	0.96	10	50–3000	Saager et al. (1991)
Upwelling	22.30°E	60.40°E	0.16	−0.014	0.97	5	5–50	
South Pacific Ocean								
SW Pacific GEOSECS 293	52.50°S	178.05°W	0.581	−0.41	0.879	19	0–5271	Boyle et al. (1976)
North Pacific Ocean								
NE Pacific (three stations)	~35°N	~130°W	0.347	−0.068	0.992	34	0–5000	Bruland (1980)
NE Pacific	30.34°N	170.36°E	0.28	0.054	0.935	21	0–5446	Boyle et al. (1976)

r, Coefficient of correlation; n, number of data points. For a given station all data for the complete water column were used, except where surface waters were excluded or treated separately as indicated (e.g. 100–4000 m vs. 0–100 m).

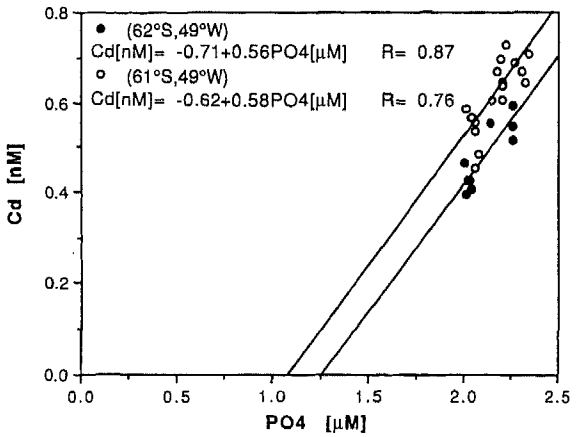

Fig. 11. The relations between Cd and phosphate at two stations in the Weddell Sea.

μM^{-1}. For the Indian Ocean sector of the Southern Ocean, Bordin et al. (1987) reported relationships between Cd and nitrate. When relying on the Redfield ratio of 16 for nitrate vs. phosphate (Redfield et al., 1963) we calculated Cd vs. phosphate to be about 0.65–0.80 nM μM^{-1} for the latter data set. Recently, Martin et al. (1990b) reported Cd values for the Drake Passage and we calculated a slope of 0.65 nM μM^{-1} from their data (Table 4).

The Atlantic Cd/P slope appears to increase from north to south, starting in the Arctic waters with a slope of 0.14 nM μM^{-1} and ending at 0.63–0.65 nM μM^{-1} in the Antarctic Ocean. In the Northwest Atlantic the slope is about 0.26 nM μM^{-1}, somewhat above the approximately 0.20 value in the Northeast Atlantic Ocean. In the Northeast Pacific Ocean, slopes are typically around 0.35 nM μM^{-1}, yet for one South Pacific station (GEOSECS Station 293) we calculated a high slope of about 0.58 nM μM^{-1}; well above the assumed global 0.35–0.4 value but comparable with the Cd/P slopes in the Antarctic Ocean.

The differences between the slopes, and especially the intercepts, indicate that the cycling of Cd and phosphate in the oceans is fairly variable from basin to basin; there is, however, a general trend. This correlation between Cd and phosphate is commonly understood to be driven by adsorptive scavenging of Cd on settling biogenic particles. This process is somewhat haphazard in nature as compared with true biological uptake of Cd within algal cells or shell material. Hence a globally uniform Cd/P relation as the outcome of scavenging processes would appear to be rather fortuitous. For example, Sherrell (1989) recently reported very different particulate Cd profiles in the North Atlantic and the North Pacific Oceans. In culture experiments, Abe and Matsunaga (1988) showed that Cd–P uptake is also dependent on the plankton species used. The latter authors further demonstrated that the

Cd/P ratios in phytoplankton largely reflect the ambient Cd/P ratio in the euphotic zone, which is high in the Antarctic region. Recently, Price and Morel (1990) found evidence of Cd substitution for Zn in diatoms at very low ambient Zn activities. Such activity may be very low indeed in oligotrophic surface waters, where some 98% of the small amount of available Zn may be bound as organic complexes (Bruland, 1989; Donat and Bruland, 1990). However, in Antarctic surface waters there is ample total dissolved Zn available (Fig. 4).

In the case of Cu, the apparent relationship with silicate has never been viewed as globally uniform (Table 3). In the Antarctic Ocean we now find a relation between Cu and silicate, with the exception of the surface values (Fig. 7). The variations in the first 100 m could be due to several processes. The very high sampling resolution (every 10–20 m) resolves variations that result from local inputs of snow or ice and uptake by (ice)algae. Contamination from the ship during sampling can never be excluded, but the smooth profile we obtained if the sea is ice covered (Fig. 4) does not support this explanation. Also, there is good agreement with the unfiltered surface samples taken far away from the ship with the zodiac. It is evident, however, that the increase in Cu concentration starts below 100 m; this is much shallower than in the North Atlantic, where the increase begins only at 2000 m. This again shows that there are local abrupt changes in water bodies. Mixing is not as gradual as in the Pacific and Atlantic Oceans. Because of this, the vertical gradients of Cu and silicate are often so low that any possible relationship is indiscernible.

Dissolved Fe levels, which range from 2 to 4 nM in the Scotia Sea and increase southwards through the Confluence towards the Weddell Sea (4–6 nM) appear adequate to sustain biological growth (de Baar et al., 1990). To date, only in Sub-Arctic North Pacific waters was Fe reported to be a limiting element in plankton growth (Martin and Fitzwater, 1988). In those surface waters, the dissolved Fe is well below 1 nM (Martin et al., 1989) and thus appears to become limiting, although there is some debate on the conclusions to be drawn from the shipboard experiments (Banse, 1990; Martin et al., 1990a). Conditions of very low dissolved Fe exist in the central ocean gyres, where, however, the nutrients are also very low and limiting in themselves. In Antarctica only those surface waters not directly influenced by atmospheric input, coastal systems and/or the ice edge would be likely to have very low dissolved Fe.

Above, we suggested that the dissolved Fe levels of 2 nM or more in the Scotia/Weddell Sea surface waters may be derived from inputs by shelf sediments; however, fine-grained erosion products may also be carried eastward from the Antarctic Peninsula and Bransfield Strait into our research area. During the same EPOS 2 expedition, F. Dehairs (personal communication, 1991) found very high levels of suspended particulate Al at most of our sta-

tions. Westerlund and Öhman (1991b) have reported a small data set for particulate Fe and Al in the southern part of the Weddell Sea. In these particles the Fe contents range from about 1 to about 50 nM. The Fe/Al ratio is fairly uniform at about 0.73 ($r=0.97$ for 23 samples), which is close to the commonly assumed crustal abundance ratio of 0.68 (Taylor, 1964). When applying an Fe/Al ratio of 0.73 to the particulate Al results of EPOS 2 (F. Dehairs, personal communication, 1991) one arrives at particulate Fe concentrations in the approximate range of 0.5–20 nM. Only partial dissolution of such material would provide dissolved Fe for plankton uptake. Another factor that may explain the higher Fe concentrations are the huge melting icebergs found in this area, which contain remains of terrestrial material. Martin et al. (1990b) reported initial ice Fe concentrations of 26 nM kg^{-1}. Some of the particulate Al (and Fe) collected by F. Dehairs (personal communication, 1991) may also have been brought in by icebergs. Finally, the Fe content of ice algae (0.05% Fe; R.F. Nolting, A.J. van Bennekom and J. De Jong, unpublished data) released from melting ice cannot be neglected.

CONCLUSIONS

Levels of dissolved Cd and Cu are very similar to those reported for the deep (North) Pacific Ocean. In accordance with the high nutrients, no surface depletion is observed for Cd and Cu. The Antarctic slope of Cd/P at around 0.64 nM μM^{-1} is well above the presumed oceanic 'grand average' of about 0.40 nM μM^{-1}, but is consistent with slopes published for the Indian Antarctic sector (0.68–0.82), for the Drake Passage (0.65) and the Southern South Pacific (0.58) as well as the deep North West Indian Ocean (0.50–0.87). In the light of these findings, the concept of a global Cd/P relation in deep waters has to be reconsidered in favour of recognizing considerable differences in Cd/P between ocean basins.

The deep water Cu/Si ratio is about 0.026 nM μM^{-1} in the Scotia Sea, comparable with ratios found in the North Atlantic Ocean, North West Indian Ocean and central North Pacific Ocean.

Dissolved Fe levels at 2–8 nM are adequate to sustain biological growth. Over the shelf, dissolved Fe is an order of magnitude higher at approximately 60 nM. Major sources of dissolved (and particulate) Fe are the extensive shelves, as well as inputs through iceberg transport.

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